Short communication

Effect of heat treatment of electrodes on direct borohydride-hydrogen peroxide fuel cell performance

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HIGHLIGHTS

- Heat treatment enhanced the hydrophilic nature of catalyst layers.
- Significant improvement in DBPFC performance was observed after heat treatment.
- Catalyst utilization was increased due to a hydrophilic catalyst layer.

GRAPHICAL ABSTRACT
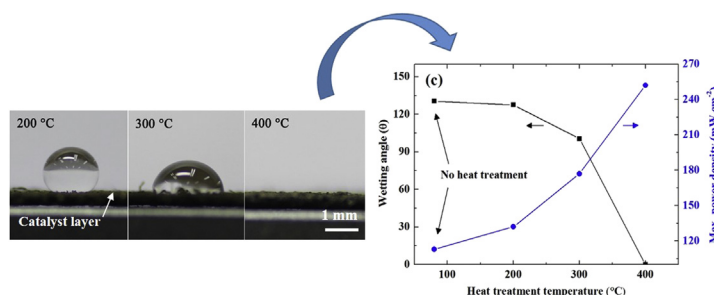
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ABSTRACT

This work investigates the effect of heat treatment of electrodes on the performance of a direct borohydride-hydrogen peroxide fuel cell (DBPFC). The electrodes are prepared by direct deposition of catalyst onto the surface of a micro porous layer (MPL) supported by a backing layer. The MPL is composed of multi-walled carbon nanotubes (MWCNT) while the backing layer is made of carbon cloth. Palladium and gold are sputter-deposited as anode and cathode catalysts, respectively. After heat treating electrodes at 400 °C in air atmosphere, the maximum power density of the DBPFC is significantly improved from 113 to 267 mW cm^{-2} at 25 °C. Long-term DBPFC performance is improved as well. The apparent improvement of the performance is due to the enhanced hydrophilic nature of catalyst layers as a consequence of heat treatment so that the utilization of catalysts is improved. The hydrophilic nature of the electrodes is from the decrease in concentration of hydrophobic fluorocarbon groups in the catalyst layers. Although heat treatment involves minor disruption of catalysts, the transition of water affinity in the catalyst layers far outweighed its influence which was demonstrated by the improved DBPFC performance.

1. Introduction

The direct borohydride-hydrogen peroxide fuel cell (DBPFC) is a potential alternative power source for air independent propulsion systems [1,2]. Initial and long-term performances of DBPFCs, however, remain insufficient for such applications. This is partially due to the low performance of the electrodes where low electrochemical activity of the catalysts [3,4], poor selectivity toward the direct oxidation and reduction of borohydride and hydrogen peroxide [5–8], or cathode catalyst poisoning are problems [9]. Low utilization of catalysts in the catalyst layers could be another cause of low electrode performance [10,11].

In the DBPFC, since both fuels and oxidants are supplied as ionic liquids [12], catalyst utilization is affected by the affinity between the catalyst layer and liquids. The use of Nafion ionomer in current

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state-of-the-art DBPFC electrode catalyst layers [4,13,14], however, seems to be hindering this affinity due to the partially hydrophobic nature of Nafion [11]. Such evidence is found in recent studies on direct liquid fuel cells such as the direct methanol fuel cell (DMFC) and direct borohydride fuel cell (DBFC). Joghee et al. [10] found that an improved hydrophilic character of the Nafion ionomer in the DMFC anode catalyst layer improved utilization of catalysts, which led to performance improvement. They treated the anode at high anodic potential, improving the Nafion ionomer–catalyst interface. Choudhury et al. [11] found that using hydrophilic chitosan chemical hydrogel instead of Nafion ionomer as a binder in the DBFC anode catalyst layer improved electrochemical performance. It is hypothesized that an enhanced hydrophilic nature of catalyst layers in both anodes and cathodes will improve the performance of the DBPFC. No such studies, however, have been reported in DBPFC.

The heat treatment of electrodes is proposed to improve DBPFC performance by changing the hydrophilic nature of catalyst layers and improving their wettability in liquid reactants. The electrodes were prepared by direct deposition of catalyst onto the surface of a micro porous layer (MPL) supported by a backing layer. The MPL was composed of multi-walled carbon nanotubes (MWCNT) while the backing layer was made of carbon cloth. Palladium (Pd) and gold (Au) were sputter-deposited as anode and cathode catalysts, respectively. After heat treating electrodes at 400 °C in air atmosphere, the hydrophilic nature of the catalyst layers were improved. This resulted in significant improvement in both initial and long-term DBPFC performances owing to an improved utilization of catalysts in the catalyst layers. Energy-dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) were done to investigate the effect of heat treatment on catalyst layer properties and its influence on DBPFC performance.

2. Experimental details

2.1. Preparation of electrodes by heat treatment

The MPL was first coated on a carbon cloth (Fuel cell earth, USA) backing layer. The details are as follows. An MPL slurry consisting of MWCNTs (Carbon nano-material technology, Korea), 5 wt% Nafion solution (D521, Dupont, USA) and isopropyl alcohol was prepared. MWCNTs were used instead of conventional XC-72 for its high electrical conductivity [15]. The weight proportion of MWCNT, Nafion ionomer and isopropyl alcohol was 2.5:1:40. The slurry was homogenized for 12 h at 300 rpm and coated on carbon cloth using a spray gun (Airbrush, Sprayworks, USA). Coating was repeated several times until the total MWCNT loading was 5 mg cm^{-2}. The MPL coated carbon cloth was dried on a hot plate set to 100 °C.

Catalysts were deposited on MPL surfaces using a sputter (SPS-TG series, Ultech co., Korea). Sputtering has been used to prepare electrodes for the DBPFC [4,5]. Pd and Au were used as anode and cathode catalysts, respectively. Both metals have high electrochemical performance as DBPFC catalysts [5,9,15]. Sputtering was done under a sputter current of 30 mA at room temperature for both metals. The catalyst loadings for the anodes and cathodes were controlled at 0.07 and 0.08 mg cm^{-2}, respectively. After sputtering, the electrodes were protonated for 30 min in a 0.5 M sulfuric acid solution and washed in distilled water. The electrodes were then dried in a convention oven for 30 min at 80 °C.

The prepared electrodes were heat treated in a furnace. Both anodes and cathodes were heat treated at the same temperature profile. The furnace temperature was raised from 25 °C to designated temperatures of 200, 300, 400 and 500 °C at a rate of 2 °C min^{-1} to investigate the effects of the temperature on the heat treatment. After initial temperature rise, each temperature was

maintained for 30 min. During heat treatment, electrodes were exposed to ambient air. After heat treatment, electrodes were cooled down to room temperature by natural convection of ambient air. The heat treated electrodes were preserved in a nitrogen environment until use.

2.2. Catalyst layer characterization

The catalyst deposited MPL surfaces (hereinafter referred to as 'catalyst layer') were characterized by wetting angle analysis, EDS analysis and XPS analysis. Wetting angle analysis determines the hydrophilic nature of the catalyst layer surfaces. A water droplet with a volume of 10 μL was dropped onto the catalyst layer surface. A high resolution digital camera and imaging software were used to measure the wetting angle. The elemental composition of the catalyst layer was analyzed by EDS (Nova 230 FEI, USA) by scanning at three different locations for accuracy. The chemical state of the catalyst was analyzed by XPS (Sigma probe Thermo VG Scientific, UK). XPS spectral data of NIST X-ray photoelectron spectroscopy database [16] was used. Charge referencing was done to the carbon peak at 284.5 eV.

2.3. Fuel cell assembly and testing

MEAs (membrane electrode assemblies) were prepared using a Nafion 212 (Dupont, USA) membrane and electrodes. Clamping graphite flow plates on both sides of an MEA with clamping pressure of 20 kgf cm^{-2} completed the construction of the test cell. The flow plates of both anode and cathode were graphite blocks with an active area of 10.89 cm^2. Each plate had engraved serpentine channels with a square cross section of 1 mm^2.

Initial and long-term performances of electrodes were evaluated in a single fuel cell. Initial performance was evaluated by current–voltage measurements. Long-term performance of electrodes was evaluated by chronopotentiometric test. A test stand was established to measure the performance of the single cell DBPFC. Fuel and oxidizer were separately supplied by liquid pumps to the DBPFC. Liquid byproducts were collected in containers and gaseous byproducts were vented through volume flow meters (FMA series, Omega, USA). The current and voltage were recorded on a computer via a data acquisition board. All tests were done at 25 °C.

The fuel was 10 wt% NaBH$_4$ and 5 wt% NaOH solution. The oxidant was 10 wt% H$_2$O$_2$ and 5 wt% H$_3$PO$_4$ solution. NaOH and H$_3$PO$_4$ were used as stabilizers to suppress spontaneous NaBH$_4$ hydrolysis and H$_2$O$_2$ decomposition [5]. Both fuel and oxidant were supplied at constant flow rates of 10 ml min^{-1}.

3. Results and discussion

3.1. Conversion of wettability of catalyst layer

The conversion of wettability of catalyst layer by heat treatment of electrodes from hydrophobic to hydrophilic nature was investigated by wetting angle analysis. The measured wetting angles on both anode and cathode catalyst layer surfaces as a function of heat treatment temperature are shown in Fig. 1. Photographic images of water drops on the surface of catalyst layers cured at different temperatures are also shown. When the surface was hydrophobic, a greater wetting angle was observed. The wettability increases and wetting angle decreases as the surface becomes hydrophilic as heat treatment temperature gradually increases as shown in Fig. 1. The wetting angle disappeared on the catalyst layer with electrodes cured at 400 °C, implying that the surface became hydrophilic. At
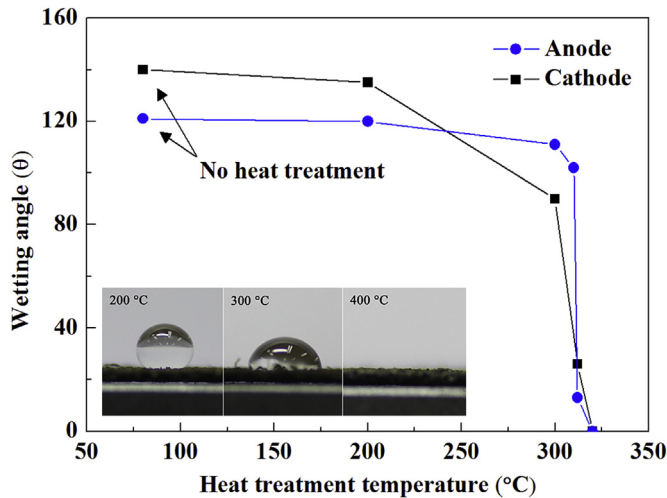
Fig. 1. Wetting angle of water on the anode and cathode catalyst layer surfaces with respect to heat treatment temperature with photographic images of water drops on the surface of catalyst layers cured at different temperatures.

temperatures beyond 325 °C, the catalyst layer surface became hydrophilic and wetting angle was zero degree for both electrodes.

The change of the wettability from hydrophobic to hydrophilic surface was due to the change of the elemental composition of the catalyst layer. The elemental composition of the surface was measured by EDS before and after the heat treatment and there was pronounced change in the composition. The elemental compositions of the catalyst layers investigated by EDS analysis are listed in Table 1 for the heat treatment temperature of 400 °C, at which the surface was observed totally hydrophilic. The prominent change was the significant reduction of fluorine concentration in both anode and cathode catalyst layers. The source of fluorine of the uncured catalyst layer was the fluorocarbon component of Nafion ionomer used as the binder in the MPL. Fluorine evaporated by curing in the oven at high temperature and its concentration dropped to nearly 8% of its initial value in both of the electrodes. The decrease in fluorine concentration was due to a thermal decomposition of Nafion ionomer in the catalyst layers. Fluorocarbon groups (C—F) in Nafion are stable up to 420 °C in normal operating conditions [17]. The decomposition of fluorocarbon in this study at a temperature below 420 °C was due to activation by the catalyst deposited on the electrode surface. The oxygen concentration also increased in both catalyst layers after heat treatment. The anode side catalyst layer showed a higher increase in oxygen concentration than the cathode side catalyst layer. XPS results confirmed that this was due to the oxidation of palladium nanoparticles in the anode catalyst layer [18]. Gold of the cathode side was not oxidized. The increase in oxygen concentration in both electrodes is partially due to the oxidation of

MWCNT forming hydrophilic functional groups [19]. Since fluorocarbon groups in the Nafion ionomer are hydrophobic [10,11], it was concluded that the enhanced hydrophilic nature of the catalyst layers was due to a decrease in hydrophobic fluorocarbon groups and increase in hydrophilic functional groups in the catalyst layers.

Control experiments were conducted to separate the combined effects of the ionomer, carbon support and catalyst and determine the dominant factor that enhanced the hydrophilic nature of catalyst layers. Firstly, the influence from the MPL and catalyst was compared. A blank electrode consisting of carbon cloth and MPL without catalyst deposition was prepared and subjected to heat treatment. Complete wetting was observed at 325 °C with both the blank electrode and electrode loaded with catalyst, which implied that the existence of the catalyst on the electrode did not affect the wettability. Secondly, the effects of fluorocarbon decomposition and carbon oxidation were compared. A blank electrode of MWCNT cured at 400 °C was prepared and subjected to heat treatment. Both cured and uncured MWCNT electrodes showed the same wettability at 325 °C, which implied that oxidation of MWCNT did not increase the wettability. The hydrophilic tendency of cured MWCNT was suppressed by Nafion ionomer by slurry preparation. Therefore, neither changes in catalyst nor oxidation of MWCNT caused the transition of the wettability of the electrode. It was concluded that the transition of the electrode to hydrophilic nature by heat treatment was largely due to the reduction of hydrophobic fluorocarbon groups in the catalyst layers.

3.2. MEA performance evaluation

The current—voltage curves of the single cell DBPFC with curing temperature of electrodes are shown in Fig. 2(a) and (b). The performance of the single cell DBPFC increased with curing temperature up to 400 °C. The maximum power density increased from 112 mW cm^{-2} of uncured electrodes to 264 mW cm^{-2} of electrodes cured at 400 °C. Increase of current densities below 100 mA cm^{-2} was by the improvement in activation overpotential [20]. The slopes of the voltage in Fig. 2(a) were similar for the test conditions beyond the current density of 100 mA cm^{-2}, because the ohmic overpotentials were similar. The single cell performance abruptly deteriorated, when the heat treatment temperature increased further to 500 °C. The oxidation of carbon support and electrodes decreased the active surface area and resulted in poor single cell performance. It was concluded that there was an optimum curing temperature of heat treatment that was 400 °C in the present case. The average wetting angle on the catalyst layer and the maximum power density of a single cell DBPFC with the specific catalyst layer as a function of heat treatment temperature are shown in Fig. 2(c). As the wetting angle decreased, the maximum power density increased to its maximum at minimum wetting angle representing the hydrophilic surface.

The long-term performance test of the single cell DBPFC with electrodes cured and uncured at 400 °C are shown in Fig. 3. The voltage was monitored under a constant load of 50 mA cm^{-2}. During the first 4 h, the output voltage with the uncured electrodes monotonously decreased while the output voltage with the cured electrodes remained stable. The better performance with the cured electrodes is likely due to a better liquid transport property. As the test progressed, gas bubbles and byproducts were produced on the electrode surface. While they remained on the electrode surface with the uncured electrodes preventing electrochemical reaction, the cured electrodes with hydrophilic nature effectively removed them with incoming reactants. After 6 h, both electrodes showed a rapid decrease in output voltage. Inspection of the electrodes after operation for hours revealed partial detachment of catalyst and

Table 1
Atomic wt% of elemental compositions of catalyst layer surfaces before and after heat treatment at 400 °C.

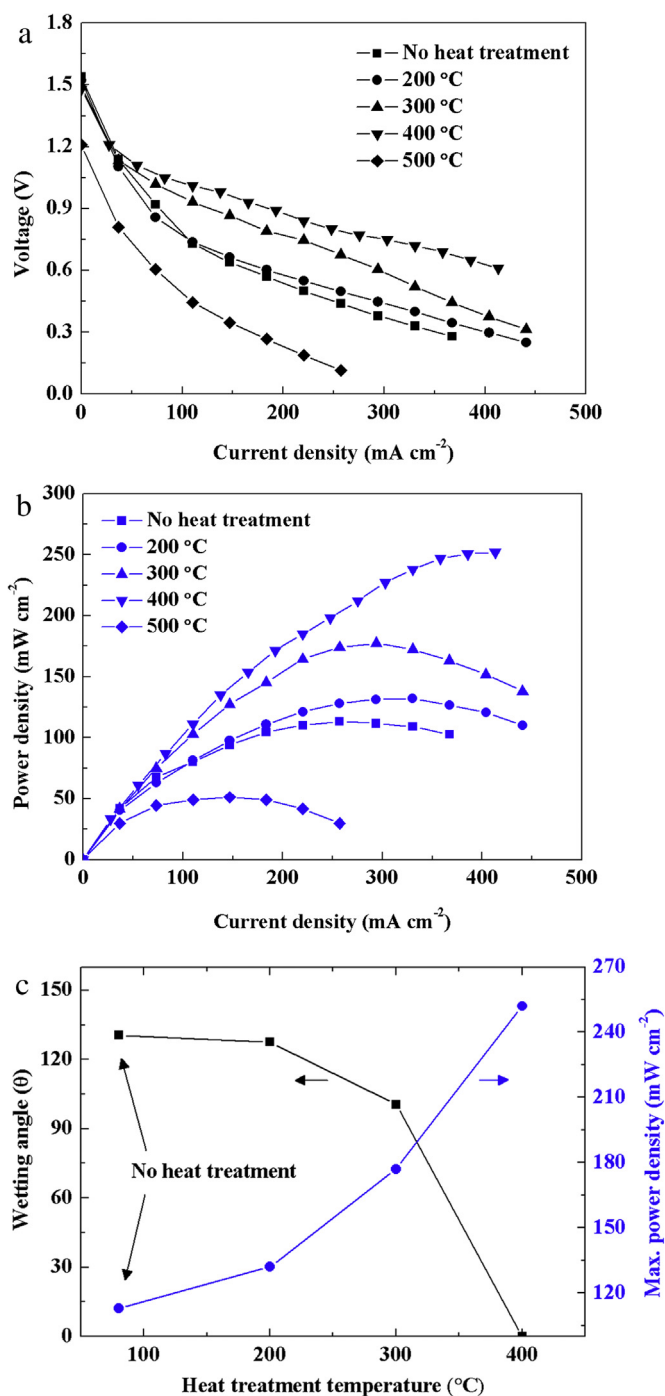|	Anode		Cathode	
	No heat treatment	Heat treatment at 400 °C	No heat treatment	Heat treatment at 400 °C
C	54.7	71.7	66.1	85.2
O	8.3	16.5	6.3	8.4
F	25.0	2.0	21.9	1.7
S	1.9	1.4	1.5	1.3
Metal catalyst	10.1	8.4	4.2	3.4

Fig. 2. (a) Voltage and (b) power density curves of MEAs using electrodes heat treated at different temperatures and (c) the average wetting angle on the catalyst layer and the maximum power density of a single cell DBPFC with the specific catalyst layer as a function of heat treatment temperature.

byproduct accumulation on the cathode that eventually blocked the oxidant flow channel. As a result, the pressure of the flow channel and output voltage fluctuated after 8 h of operation.

The effect of heat treatment on electrodes prepared by conventional wet impregnation method was investigated. Pd/MWCNT and Au/MWCNT electrocatalysts were prepared as anode and cathode electrocatalysts, respectively, using the $NaBH_4$ reduction method as described by Oh et al. [15]. Catalyst slurries were prepared by mixing the prepared electrocatalysts with Nafion ionomer with isopropyl alcohol as the solvent. The weight proportion of
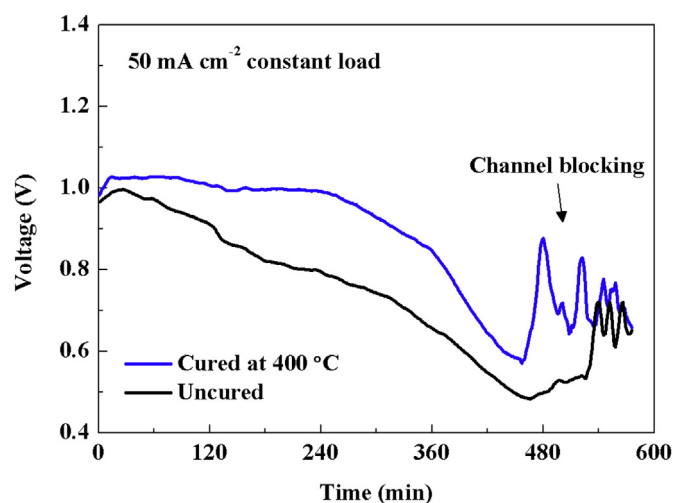

Fig. 3. Chronopotentiometric test results of MEAs 1 and 4. MEA1 uses electrodes with no heat treatment. MEA4 uses electrodes with heat treatment at 400 °C. Applied current: 50 mA cm^{-2}.

MWCNT, Nafion ionomer and isopropyl alcohol was 2.5:1:40. Catalyst slurries were then coated and dried on carbon cloths. The MWCNT and catalyst loadings were 5 and 1 mg cm^{-2}, respectively. The voltage and power density of the single cell DBPFC using electrodes with catalyst layers prepared by wet impregnation before and after heat treatment at 400 °C are shown in Fig. 4. The effect of heat treatment was consistent even with the electrodes prepared by wet impregnation method. The maximum power density increased from 121 mW cm^{-2} to 234 mW cm^{-2}. It was concluded that transition of wettability of the catalyst layers was mainly affected by the surface composition of Nafion ionomer by heat treatment.

3.3. XPS analysis of catalyst

The effect of heat treatment on the nature of catalyst itself was investigated by XPS analysis. The XPS spectra of Pd 3d on the anode side catalyst layer cured at different temperatures are shown in Fig. 5(a). Before heat treatment, strong peaks of palladium oxide (PdO) were detected at 335.6 eV (3d5/2) and 341.3 eV (3d3/2). At heat treatment temperatures of 300 and 400 °C, strong peaks of
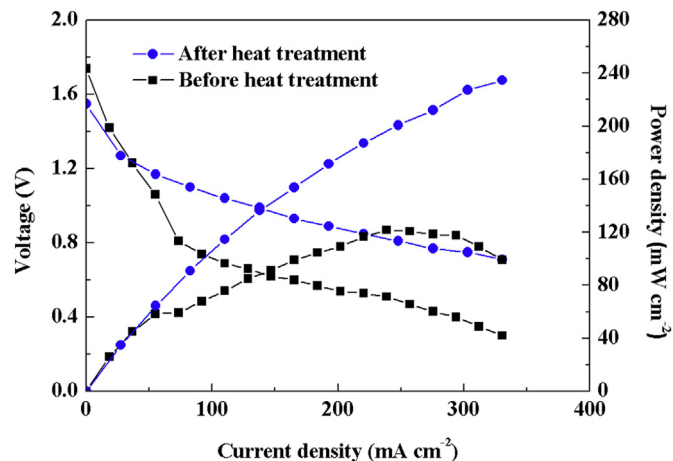

Fig. 4. Voltage and power density curves of electrodes prepared by wet impregnation before and after heat treatment at 400 °C.
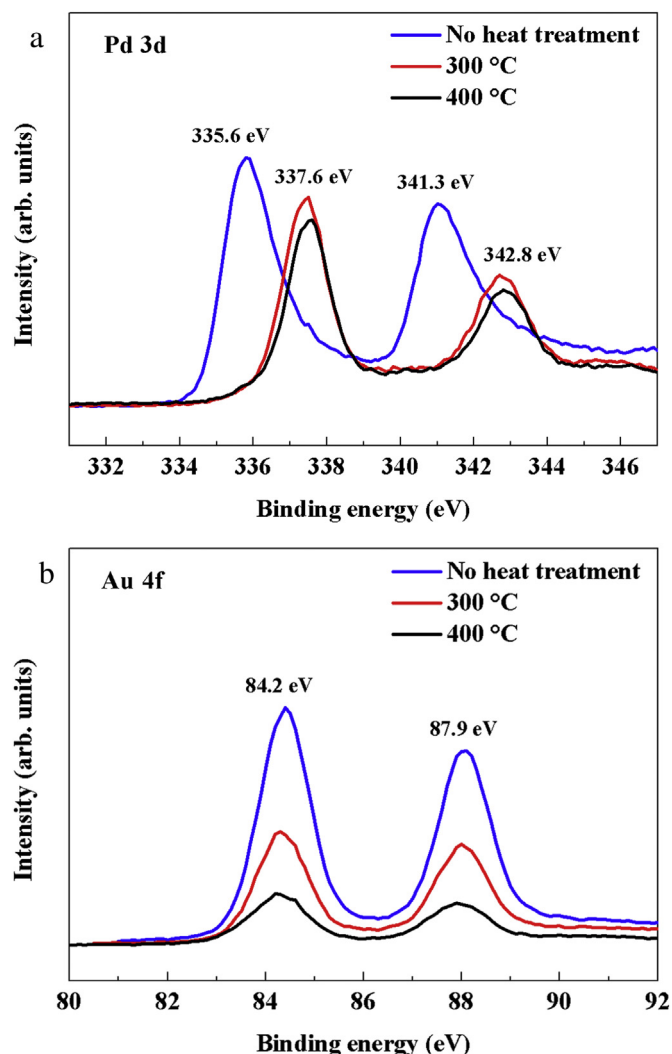
Fig. 5. XPS spectra of (a) Pd 3d on the anode and (b) Au 4f on the cathode heat treated at different temperatures.

palladium oxides (PdO$_x$) were detected at 337.6 eV (3d5/2) and 342.8 eV (3d3/2). The initial oxidation of palladium was due to the protonic treatment of the electrodes prior to the heat treatment. Heat treatment further accelerated the oxidation of palladium. The XPS spectra of Au 4f on the cathode side catalyst layer cured at different temperatures are shown in Fig. 5(b). Peaks of metallic gold at 84.2 eV (4f7/2) and 87.9 eV (4f5/2) did not depend on the heat treatment temperature. The signal intensity, however, decreased with increasing heat treatment temperature. The decrease in Au peak intensity was due to an agglomeration of Au nanoparticles, which was confirmed from scanning electron microscope images of the catalyst layer surface (Fig. 6). Consequently, the minor disruption of catalysts after heat treatment possibly affected DBPFC performance. It seems the enhanced hydrophilic nature of the catalyst layers, however, far outweighed its influence which was demonstrated by the significantly improved DBPFC performance.

4. Conclusions

In order to improve the performance of a single cell DBPFC, electrodes with enhanced hydrophilic nature were prepared by heat treatment. The short and long-term performance of the electrodes were tested. The electrodes were prepared by direct
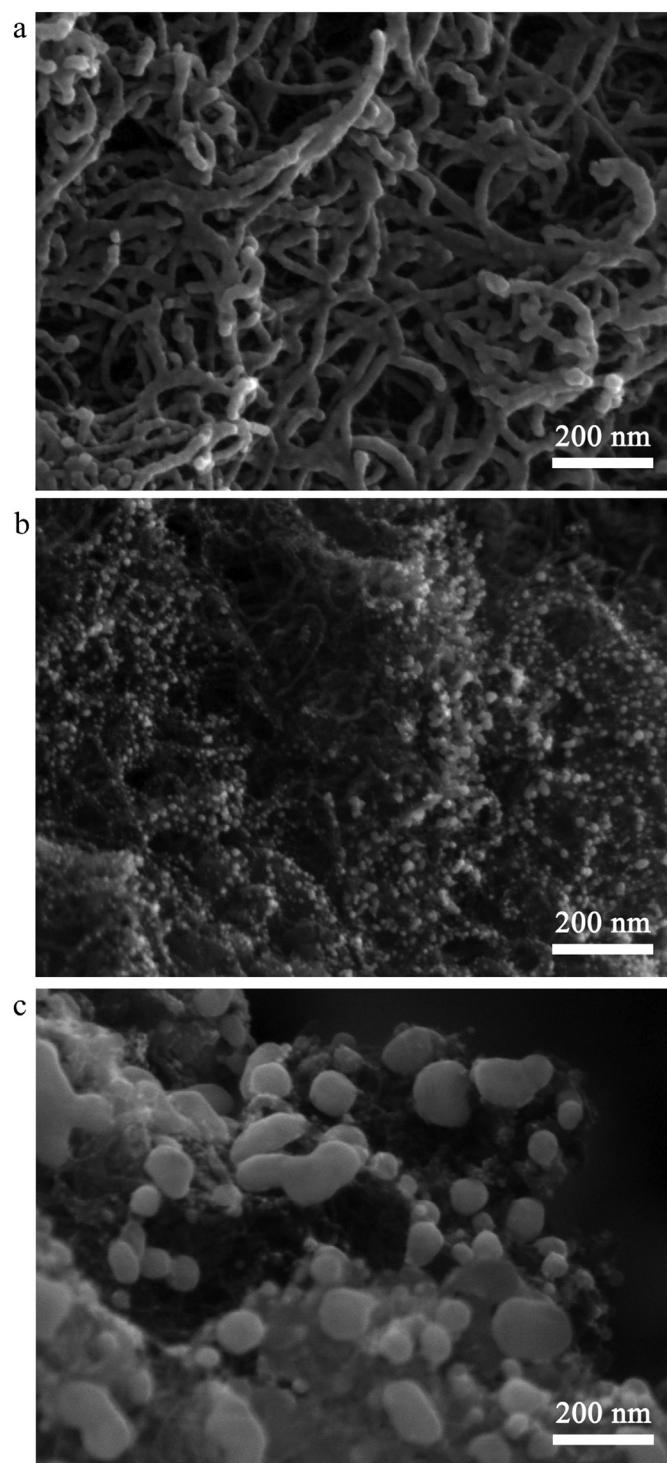

Fig. 6. SEM images of the cathode catalyst layer surface with respect to curing temperature. (a) No heat treatment, (b) 300 °C, and (c) 400 °C.

deposition of catalyst onto the surface of a micro porous layer (MPLs) supported by a backing layer. Heat treatment markedly improved the short-term performance. The maximum power density increased from 112 mW cm^{-2} of uncured electrodes to 264 mW cm^{-2} of electrodes cured at 400 °C in air environment. Long-term performance was improved as well. The improved performance of the electrodes was due to the suppressed hydrophobic nature of the catalyst layers as a consequence of heat treatment

that improved liquid transport and utilization of catalysts. Although heat treatment involved minor disruption of the catalyst, the transition of water affinity in the catalyst layers far outweighed its influence, which was demonstrated by the improved DBPFC performance.

Acknowledgements

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